



Enhanced thermal resistance of phenolic resin composites at low loading of graphene oxide



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ABSTRACT

By incorporating graphene oxide (GO) into phenolic resin (PR), GO/PR composites were prepared, and the effects of the content and reduction degree of GO on thermal resistance of GO/PR composites were studied. The peak degradation temperature of the PR was increased by about 14 °C with GO which was heat treated. The char yield of GO/PR composite at a GO weight fraction of 0.5% was about 11% greater than that of PR. The interactions such as covalent bonds and π - π stacking between GO and PR were regarded as the main reason for the enhancement. Located at the GO–PR interface, GO effectively anchored and structured PR molecular near the surfaces of GO sheets, and thus facilitated the formation of char. The superiority of GO/PR composites over PR in terms of thermal properties enhancement should also be related to the promoting graphitization by the addition of GO.

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1. Introduction

Phenolic resin (PR) is an important resin matrix used for ablative composites, offering high reliability under severe conditions. In order to meet the requirements of the ablative materials for aerospace, the modified PR with advanced thermal resistance has been developed by incorporating carbon materials, such as carbon nanofibers, carbon nanotubes and graphite [1–4]. In spite of the observed thermal stability reinforcing effect, the carbon materials were difficult to disperse in PR matrix, and thus the expected improvements in processabilities and mechanical properties by incorporating carbon materials were not fully realized.

The polymer-based composite with graphene oxide (GO) have attracted tremendous attention recently due to the impressive performances of GO, including good dispersion, strong interactions between GO and PR matrix, and the modification effects on the thermal resistance of polymer [5–8]. The GO consists of covalently attached oxygenated functional groups such as hydroxyl, epoxy, carbonyl and carboxyl groups which made GO easy to disperse in organic solvent and polymer matrix [9,10]. Furthermore, the GO can be chemically functionalized and reduced for the preparation of polymer matrix composites so as to improve the thermal

resistance of the polymer. Verdejo et al. [11] have prepared functionalized GO sheet filled silicone porous composites and the onset and the peak degradation temperatures ($T_{d,max}$) were increased by up to 16 °C and 55 °C, respectively. Xu et al. [12] have reported the preparation of poly(vinyl alcohol) (PVA)/GO composite films which showed a $T_{d,max}$ of 36 °C higher and slower decomposition rate than that of pure PVA.

In the present work, the GO/PR composites with high thermal resistance were prepared by introducing GO into PR matrix, which provided a new class of GO/polymer composite for ablative materials. The effects of content and reduction degree of GO on the thermal resistance of the GO/PR composites were studied. In fact, the pyrolysis mechanism of GO/PR composites was altered due to high specific surface of GO sheet and the interaction between PR and GO sheet, which resulted in high thermal properties of GO/PR composites.

2. Experimental

2.1. Materials

The PR, which was a thermosetting resin, was supplied by Xi'an Aerospace Composite Materials Research Institute. The natural flake graphite (200 meshes) was supplied by Qingdao Hengruimifeng Zhipin Co., Ltd. The other chemicals were of analytical grade from Xi'an Chemical Reagent Factory.

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2.2. Preparation of GO dispersion

The GOs with different reduction degrees were obtained by treating in different temperatures [10,13]. The graphite oxides were prepared by Hummers' method [14], dealt with at a certain temperature (120, 200 or 250 °C) under nitrogen (N₂) atmosphere for 4 h in the tube furnace (SGM6812B5, Luoyang Sigma Instrument Manufacture Co., Ltd.). The graphite oxide was dispersed in ethanol to create a 0.2 mg/mL graphite oxide dispersion and exfoliation of graphite oxide to GO was achieved by ultrasound using an ultrasonic cleaning bath (model ACQ-600, Shaanxi Ultrasonic Instrument Company) for 2 h, with a power of 250 W (determined by the electrical method) and operated at 27 kHz. The GOs with different reduction degrees were named as GO120, GO200 and GO250, according to the processing temperatures of 120, 200 and 250 °C, respectively.

2.3. Preparation of GO/PR composites

The GO/PR composites were prepared by dispersing GO in the PR solution (50 wt% in ethanol). The PR solution was added into the 0.2 mg/mL of GO dispersion according to the designed compositions, and then dispersed by ultrasound for 0.5 h at room temperature to prepare dispersion of GO/PR. The GO/PR dispersion was poured into a glass culture dish and allowed to evaporate slowly overnight at room temperature, and then dried in vacuum at 50 °C under the vacuum of 0.095 MPa, and was weight every 30 min till no weight loss.

The GO/PR composites were cured at 120 °C for 2 h, 165 °C for 4 h, and 220 °C for 2 h in an air-circulating oven according to the differential scanning calorimetry (DSC) analysis. The GO/PR composite which contained 0.1, 0.3, 0.4, 0.5, 1.0, 1.5 and 2.0 wt% of GO was referred to as GO/PR-0.1, GO/PR-0.3, GO/PR-0.4, GO/PR-0.5, GO/PR-1.0, GO/PR-1.5 and GO/PR-2.0, respectively.

2.4. Measurements

The Fourier transformed infrared (FT-IR) spectra of all the samples were recorded between 500 and 4000 cm⁻¹ from KBr pellets by Bruker Tensor 27 Spectrophotometer. The Ultraviolet–visible (UV–vis) absorption spectra were recorded using a 1 cm path length quartz cuvette with ethanol as the reference on a U-2001 UV/vis Spectrophotometer (Hitachi). The average particle size of GO sheet was measured by Malvern Zetasizer Nano-ZS particle analyzer.

The DSC was performed on a NETZSCH DSC 200PC (NETZSCH Corporation, Germany) with a heating rate of 10 °C/min from room

temperature to 300 °C using N₂ purge and an empty aluminum pan as a reference. A hermetically sealed pan was used for all DSC tests. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209C (NETZSCH Corporation, Germany), and the measurements were performed in with a heating rate of 10 °C/min from room temperature to 800 °C using a N₂ flow rate of 60 mL/min.

The surfaces of PR and GO/PR composite were coated with a thin gold layer through vacuum sputtering, and subjected to morphology examination on a field-emission Scanning Electron Microscope (SEM, JSM-7000F). Raman spectra were recorded from 200 to 2000 cm⁻¹ on a Confocal Raman Microprobe (HORIBA Jobin Yvon) using a 514 nm argon ion laser. X-ray diffraction (XRD) patterns were collected on a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm).

3. Results and discussion

3.1. Structures of GO and GO/PR composites

The aromatic structure was partially restored and the reduction degree of GO was improved by heat treatment. The FT-IR spectrum of GO120 illustrated the presence of C–O ($\nu_{\text{C-O}}$ at 1060 cm⁻¹), C–O–C ($\nu_{\text{C-O-C}}$ at 1100 cm⁻¹), C–OH ($\nu_{\text{C-OH}}$ at 1396 cm⁻¹), and O–H ($\nu_{\text{O-H}}$ at 3435 cm⁻¹) originated from carboxylic acid and the O–H stretching mode of intercalated water. The peak at 1636 cm⁻¹ can be attributed to skeletal vibrations of unoxidized graphitic domains (Fig. 1). After reduction, the peaks at 1060, 1100, 1396 and 3435 cm⁻¹ were attenuated in the GO200 and GO250 spectra (Fig. 1a), demonstrating the disappearance of some oxygenated functional groups and the restoration of the π -conjugated network of GO sheet [15]. This is supported by the redshift of UV–vis spectra. In UV–vis spectra, the absorption peak of GO at 232 nm redshifted to 273 nm with improving the temperature,

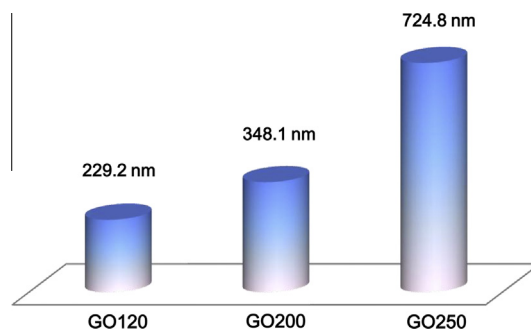


Fig. 2. Average particle size of GO sheets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

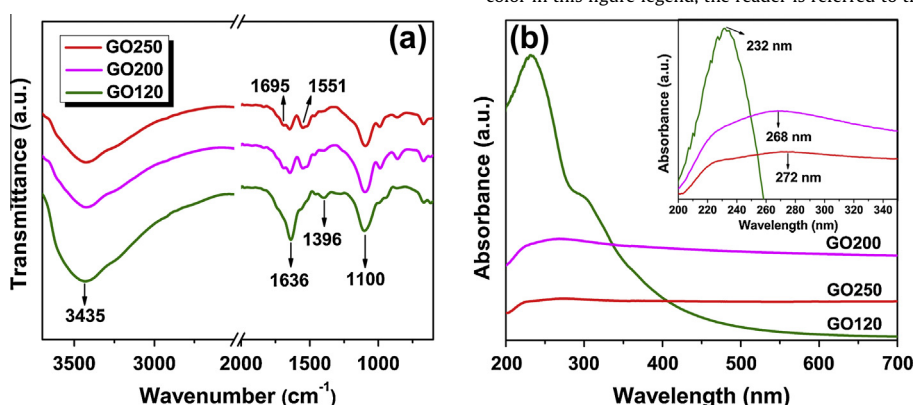


Fig. 1. FT-IR (a) and UV–vis (b) spectra of GO with different degree of reduction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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